

The Photo-electric Action of X-Rays.

By O. W. RICHARDSON, F.R.S., Wheatstone Professor of Physics,
University of London, King's College.

(Received December 28, 1917.)

The fundamental law of photo-electric activity states that

$$\frac{1}{2}mv^2 = h\nu - w, \quad (1)$$

where the left-hand side represents the maximum kinetic energy of the liberated electrons, h is Planck's constant, ν is the frequency of the exciting light, and w is a constant which measures the work necessary for an electron to escape from the substance, and whose value is characteristic of the material under consideration. The equation (1) was first given by Einstein* as a deduction from the view that the energy of radiation was distributed in discrete quanta. However, I succeeded† in showing that it followed from Planck's radiation formula; so that it evidently has a wider basis than the restricted and doubtful hypothesis used by Einstein.

On the experimental side the evidence for several years was somewhat conflicting, but in 1912 I showed‡ as a result of experiments made in collaboration with Dr. K. T. Compton, that the equation represented the photo-electric behaviour in the visible and in the ultra-violet as far as $\lambda = 2 \times 10^{-5}$ cm., for the metals sodium, aluminium, magnesium, zinc, tin, and platinum as accurately as it could be determined. The experiments also showed that the differences in the values of the constants w for different metals were connected with the corresponding contact potentials V by the relation

$$w_n - w_m = e(V_n - V_m). \quad (2)$$

This was confirmed both by direct measurement of the energy of the emitted electrons, and by determining the threshold frequencies ν_m given by the obvious relation

$$w_m = h\nu_m. \quad (3)$$

When these experiments were started I thought it improbable that equation (1) would turn out to be correct, on account of the very grave objections to the form of quantum theory on which it had up to that time been based by Einstein. After making the experiments I felt that there

* 'Ann. d. Physik,' vol. 17, p. 145 (1905).

† 'Phys. Rev.,' vol. 34, p. 146 (1912); 'Phil. Mag.,' vol. 24, p. 570 (1912).

‡ 'Science,' vol. 35, p. 783 (1912); 'Phil. Mag.,' vol. 24, p. 575 (1912).

was no reasonable doubt of its entire validity. I confess that this view has not been shared by all the more recent writers on the subject. However, as it has been confirmed by the independent experiments of Hughes,* and by the very careful critical work of Millikan,† who has shown that the equation can be used to determine the value of h with very great accuracy, there can at the present time be no doubt of its validity.

In the X-ray region the researches of Sadler,‡ Beatty,§ Whiddington,|| and Moseley,¶ taken together,** have shown that the *maximum* energy of electrons liberated by X-rays of frequency ν is very closely represented by

$$\frac{1}{2}mv^2 = h\nu. \quad (4)$$

This relation is evidently consistent with (1), since the electrons with the maximum velocity will come from the more superficial parts of the atom, and for such electrons w is negligible in comparison with $h\nu$ in the case of X-rays. The fact that (4) represents the experimental results with sufficient accuracy cannot, therefore, be considered an argument against equation (1) being the complete expression of the facts in this case.

The study of the generation of X-rays by the impact of electrons of various velocities has shown that equation (4), and in all probability equation (1), operates both ways; that is to say, there is an upper limit to the frequency of the radiation generated by the impact of electrons with energy $\frac{1}{2}mv^2$ which is given by equation (1). This can be deduced from the earlier experiments of Kaye†† and Whiddington,‡‡ and has been confirmed by the recent very accurate work of Duane and Hunt.§§. There is evidence that the same condition governs the excitation of ordinary spectral lines by means of electron impacts of definite velocity, but in this case secondary complications arise which make the phenomena less easy to disentangle.

The foregoing statements and facts show that equation (1) represents a condition possessing a very high degree of generality. It evidently embraces the whole gamut of the radiation scale in its interaction with every type of matter. So far, it has only been demonstrated as a limiting condition. That is to say, when matter is subjected to the action of radiation of

* 'Phil. Trans.,' A, vol. 212, p. 205 (1912).

† 'Phys. Rev.,' vol. 7, pp. 18, 355 (1916).

‡ 'Phil. Mag.,' vol. 19, p. 337 (1910).

§ 'Phil. Mag.,' vol. 20, p. 320 (1910).

|| 'Roy. Soc. Proc.,' A, vol. 86, pp. 360, 370 (1912).

¶ 'Phil. Mag.,' vol. 27, p. 703 (1914).

** Richardson, 'Electron Theory of Matter,' Chap. XIX.

†† 'X-Rays,' 1914 edition, p. 124.

‡‡ 'Roy. Soc. Proc.,' A, vol. 85, p. 323 (1911).

§§ 'Phys. Rev.,' vol. 6, p. 166 (1915).

frequency ν , no electron ever acquires a total energy, kinetic ($\frac{1}{2}mv^2$) and potential (w), in excess of $h\nu$. On the other hand, there is nothing in the evidence referred to above which can be said to contravene the view that equation (1) completely represents the transference of energy between radiation and the electrons contained in matter, and that it is not merely confined to a statement of the limiting velocities or frequencies attainable in such interchanges. The experimental evidence necessarily largely relates to solid substances, and, before an electron can escape from such a substance, it must, as a rule, lose a great deal of its energy in atomic encounters. So far as the results available have been analysed, or are capable of being analysed, they have been found to be consistent with the view that individual energies of electrons below the limiting value all arise from such losses. The reversibility of the equation likewise suggests that it is a true equation, and not an inequality. Moreover, the experiments of C. T. R. Wilson,* on the photography of the tracks of the emitted electrons in gases, indicate that for monochromatic radiations they would consist of a limited number of definite lengths rather than a series extending from zero to an upper limit. Certain theoretical arguments might lead us to contemplate the occurrence of energies corresponding to integral multiples of $h\nu$, but the group of facts under consideration has afforded no evidence of their existence up to the present. The evidence so far considered, and it is drawn from a very wide field, points to the absorption and emission of radiation, in so far as it is concomitant with emission or absorption of electrons, that is to say, with the transference of energy from the radiant to the material form, as taking place primarily in whole quanta, and nothing but whole quanta.

In the Bakerian Lecture for 1916 Barkla has adduced data on the electron emission especially associated with the emission of the K series of fluorescent X-radiations, from which he concludes that the absorption of radiation associated with such emissions is not confined to whole quanta, but may take place in amounts which vary continuously between one quantum and two quanta. In fact, on p. 359, he states: "There is no evidence of absorption of X-radiation in whole quanta, though the conditions are frequently such as to give an approximation to this."

There is no doubt, however, that the absorption and emission of X-rays, more especially by heavy atoms, is a complex phenomenon, and it appears that the new facts, when considered critically, so far from lending support to the view that absorption of X-radiation takes place continuously, and in amounts which may vary by any fraction of a whole quantum, seem rather to be in favour of the contrary hypothesis.

* 'Roy. Soc. Proc.,' A, vol. 87.

Broadly speaking, the method of investigation employed by Barkla is to determine the ratio between the energy of the secondary K fluorescent radiation and that of the accompanying electronic radiation for a given absorption of primary X-rays of varying frequency ν . The method adopted involves the inclusion of the energies of the soft L, M, etc., radiations in the measured electronic radiant energy. If ν_K , ν_L , ν_M , etc., are the frequencies of the fluorescent K, L, M, etc., rays he finds approximately that the energy of the K fluorescent radiation is to that of the accompanying electronic and L, M, etc., fluorescent radiations as $h\nu_K : h(\nu + \nu_L + \nu_M + \dots)$. Assuming that these radiations represent the whole of the absorbed energy, this is equivalent to saying that the energy of the K fluorescent radiation is to the whole energy absorbed as $h\nu_K : h(\nu + \nu_K + \nu_L + \nu_M + \dots)$. When $\nu = \nu_K$ there is one quantum of K fluorescent radiation emitted and also one electron emitted for every two quanta of primary radiation absorbed. When $\nu_K/\nu =$ zero there is, in the limit, one quantum of K fluorescent radiation and also one electron emitted for every quantum of primary absorbed radiation. For intermediate values of ν one quantum of fluorescent K radiation and one electron are emitted as a consequence of the absorption of amounts of primary radiation which increase continuously from one to two quanta according to the frequency of the primary radiation. It is also assumed, on grounds which appear to me insufficient, that the energy of the electronic radiation is invariably equal to one quantum $h\nu$ of the primary radiation. The demonstration that there is approximately one electron emitted for each quantum of K fluorescent radiation emitted rests fundamentally on this assumption. It has been proved beyond reasonable doubt that the maximum energy of the electrons in question is approximately equal to $h\nu$, and it is not unreasonable to suppose that this magnitude will correspond closely with the actual value of the energy of one group of electrons on emission, in accordance with the argument on p. 271. On the other hand, it is to be anticipated, as will be shown below, on account of the complexity of the phenomena of X-ray emission, that in general there will be other groups of electrons for which the maximum energy may in general have any value between $h\nu$ and zero. The experiments hitherto made which bear on this point have been directed to the determination of the maximum energy of the whole group of electrons, and would not be expected to detect the simultaneous presence of groups having a less degree of maximum energy than that value. If these criticisms are correct, Barkla's interpretation of his results is open to question, and they cannot be held to prove that absorption of X-radiation takes place continuously. In any event they could hardly be held to prove the thesis, unless it were

established that the alternative hypothesis were incapable of accounting for them.

Having due regard to our knowledge of X-ray phenomena, let us consider what we should expect on the assumption that absorption takes place in whole quanta, and that the fundamental law of the matter is expressed by equation (1). We know from Barkla's researches that the emission of fluorescent X-rays is closely connected with increased absorption of the primary rays, and it follows from W. H. Bragg's* experiments that this increased absorption, connected with the K emission, does not set in until a frequency equal to that of the shortest K line has been obtained. Consequently, as has been pointed out by J. J. Thomson,† Bohr,‡ and Kossel,§ the first process involved in the emission of the K radiation is the removal of an electron from the innermost ring to a point near the surface of or outside the atom, and the various K lines result from the subsequent filling up of the gap in the innermost ring by electrons from the various outer rings.

[*Note added February 22, 1918.*—Considerations brought forward by Bohr strongly support the view that the innermost ring is the one which is concerned in the emission of the K radiations. If this position should prove to be well founded it would seem necessary to look for the origin of the more penetrating J radiations, which Barkla has recently found to be given off by atoms of relatively low atomic weight, in the displacement of electrons from the nucleus of the atom.]

If these were the only processes occurring we should have, on the quantum theory immediately under consideration, in the first place, the absorption of a quantum $h\nu$ of radiation by a K electron from the primary rays. By equation (1) this would give rise to an emitted electron having kinetic energy $\frac{1}{2}mv^2 = h\nu - w$. The energy w is only lost for the time being, and during the process of restoring the normal atom which fills up the innermost ring again, it is re-emitted in the form of K, L, M, etc., radiations whose frequencies satisfy the equation

$$w = h\nu_K + h\nu_L + h\nu_M + \dots + \epsilon. \quad (5)$$

It is possible that some small part of the energy w may be converted into radiations of long wave-length or into other forms of energy which are unable to give rise to ionisation. In that case such energy would be lost so

* 'Phil. Mag.', vol. 29, p. 407 (1915); see also Webster, 'Phys. Rev.', vol. 7, p. 599 (1916).

† 'Phil. Mag.', vol. 23, p. 456 (1912).

‡ 'Phil. Mag.', vol. 26, p. 1 (1913); vol. 34, p. 394 (1915).

§ 'Verh. d. Deutsch. Physik. Ges.', vol. 16, p. 953 (1914).

far as ionisation experiments are concerned. To take account of this possibility the quantity ϵ has been included in (5). It is to be expected that the lost energy ϵ will be small compared with $h\nu$, but that it will be relatively most important in the neighbourhood of $\nu = \nu_K$. The values of ν_K , ν_L , etc., in equation (5) are to be understood as average values, being averaged according to the frequency of occurrence of the processes corresponding to the emission of the various K, etc., lines. According to the view taken, which Kossel has shown to be in substantial accord with the known facts, in considering the restoration to the normal condition of any particular atom which has lost a K electron, one or more of the various frequencies L, M, etc., may be absent. Thus, if an electron jumps to the K ring from the next ring but one we shall get a K_β emission and no L emission but only emissions of lower frequency (M, etc.) than the L emissions, and so on. It is to be remembered that in Barkla's experiments on bromine the L and M radiations on account of their high absorbatibility cannot be distinguished from electronic radiations; so that their energy is added to the measured electronic energy.

If the foregoing were the only phenomena to be taken account of, we should have, on the view developed above, for every quantum $h\nu$ of primary radiation absorbed the following amounts of energy in other forms:

A.

- (1) Energy of K fluorescent radiation, $h\nu_K$.
- (2) Energy of true electronic radiation, $h(\nu - \nu_K - \nu_L - \nu_M - \dots) - \epsilon$.
- (3) Energy of apparent electronic radiation, $h(\nu_L + \nu_M + \dots)$.
- (4) Lost energy, ϵ .

But Barkla's experiments show that in the neighbourhood of $\nu = \nu_K$ the proportion of the absorbed energy which reappears as energy of electronic radiation is much greater than that which is indicated by the scheme A. Without understanding precisely how this emission of electronic radiation comes about, we can see that it must occur if the emission of the K fluorescent radiation is to set in as soon as the frequency of the exciting primary radiation reaches a value identical with or very close to that of the K_γ ray as Bragg's results indicate.* For a quantum $h\nu_\gamma$ of radiation of this frequency, represents

* Webster, 'Phys. Rev.', vol. 7, p. 607 (1916), from careful observations of the radiation from a rhodium anticathode, concludes that the special absorption commences exactly at the frequency of the K_γ ray, and quotes Hull as having made similar observations with tungsten and molybdenum. The energy of the electrons necessary to excite the various K rays corresponds on the quantum relation $\frac{h}{\nu}$ frequency some 1·0–1·5 per cent. higher than this value.

the work done by an electron in moving from a position in an outer ring (probably the outermost ring) to an unoccupied position in the innermost (K) ring. But the normal atom contains one electron more than that just considered, and the work to remove an electron from the K position in a normal atom to the γ position will, therefore, be greater than $h\nu_{K\gamma}$. This difference will be further accentuated by the electrostatic repulsion of the individual electrons in the outer rings, which will tend to prevent the K electrons from undergoing a displacement to the outer positions such as is a necessary antecedent to the emission of the K fluorescent radiation. These difficulties disappear if an outer electron is first removed, so that, on these grounds, it is to be anticipated that at the limiting frequency each quantum of K fluorescent radiation liberated will be accompanied by the emission of one electron from the outer layers. According to the view proposed the energy for this liberated electron must come from the absorption of one quantum of the primary radiation.

When $h\nu$ is large compared with $h\nu_K$, the energy given by the primary radiation to a K electron is large compared with the energy necessary to escape from the atom; so that it is not to be expected that the emission of a K electron in this case will be affected appreciably by the absence of a single electron from the surface layers. Thus this special emission of electronic radiation should not occur when ν becomes very great. For intermediate values of ν it is to be anticipated that it will fall away continuously from the value of one electron for each quantum of fluorescent emission at the critical frequency to zero when ν becomes infinite.

An alternative statement of this part of the position, which is possibly only a recapitulation of the experimental facts, is to say that, in connection with the intense absorption of the primary rays by electrons in the interior of the atom, which sets in as soon as ν exceeds the critical frequency, there is a special absorption of energy in the exterior layers. The increased tendency to absorb energy in the exterior layers may be caused by instability, arising from the presence of the large amounts of energy absorbed or possessing a configuration suitable for absorption in the interior layers. In any event, the emission of such electrons from the outer layers is a condition which alone admits of the liberation of K electrons at the limiting frequency. With increasing frequency, its influence becomes less and less important.

On the view just developed, there will be associated with each quantum of K fluorescent radiation emitted an emission on the average of p electrons from the outer layers of the atom. The value of p will increase from zero for $\nu = \infty$ to the value unity when ν falls to the critical frequency. The

energy absorbed from the primary radiation by these p electrons will be $p\hbar\nu$. This will give rise to the emission of p electrons, each with a kinetic energy $\frac{1}{2}mv^2 = \hbar\nu - w'$, where w' is the work for these electrons to escape from the atom. On the subsequent return of the atom to the normal condition, the energy w' will reappear as energy of soft fluorescent X-radiations such as L, M, etc., radiations, depending on the depth within the atom from which the electron has been ejected, together with, possibly, some radiation of wave-length too long to cause ionisation, which will be lost so far as the ionisation measurements are concerned, and may be represented by ϵ' . In the experiments under consideration, the energies of the soft fluorescent radiations are indistinguishable from that of the purely electronic radiation, so that, as far as the measurements are concerned, the radiation thus absorbed is represented in effect by—

B.

- (1) Energy of K fluorescent radiation = 0.
- (2) and (3) Energy of true and apparent electronic radiation = $p(\hbar\nu - \epsilon')$.
- (4) Lost energy = $p\epsilon'$.

On this view, the complete disposition of the energy will be given by adding the corresponding quantities in schemes A and B together, and the various measured energies, if we do not distinguish between the true electronic energy and that arising from soft fluorescent X-radiations, as these are not separated by the measurements, will be in the proportion of the numbers given in the following scheme (C):—

C.

$$E_A = \text{Energy absorbed from primary radiation} = (1+p)\hbar\nu.$$

$$E_K = \text{Energy of K electronic radiation} = \hbar\nu_K.$$

$$E_e = \text{True + apparent energy of electronic radiation}$$

$$= \hbar[(1+p)\nu - \nu_K] - \epsilon - p\epsilon'.$$

$$E_l = \text{Lost energy} = \epsilon + p\epsilon'.$$

It will be observed that the relation between E_e and E_A is more complex than that between E_K and E_A on account of the possible effect of the lost energy having to be taken into consideration. From the Table given by Barkla on p. 345 of the Bakerian Lecture for 1916 it appears that the lost energy may possibly exceed 12 per cent. of the total absorbed energy in the neighbourhood of the limiting frequency, but the data are too scanty and irregular to form any reliable conclusions as to this matter. For this

reason, in testing the application of the theory to the experimental data I shall keep to the simpler relation between E_K and E_A .

As regards the function p all that we are entitled to expect, so far, is that it will be a function of ν , involving parameters depending on the structure of the particular atom concerned, which approaches the value zero as ν approaches infinity and which approaches the value unity as ν approaches the value of the critical frequency $\nu_{K\gamma}$. A very general function satisfying these conditions is

$$p = e^{-\sum \alpha_q [(\nu - \nu_{K\gamma})/\nu_{K\gamma}]^{\sigma q}} \quad (6)$$

where $q = 0, 1, 2, 3$, etc., the α_q 's are constant coefficients, and σ may be a constant proper fraction or unity. From the relations (C) we have

$$\frac{E_K}{E_A} = \frac{\nu_K}{(1+p)\nu} = \frac{\lambda}{(1+p)\lambda_K} = f \quad (7)$$

and

$$\frac{\partial f}{\partial \left(\frac{\lambda}{\lambda_K} \right)} = \frac{1}{1+p} \left[1 - \frac{p}{1+p} \sum \alpha_q \frac{\lambda_{K\gamma}}{\lambda} \left(\frac{\lambda_{K\gamma} - \lambda}{\lambda} \right)^{\sigma q - 1} \right], \quad (8)$$

and at the critical value $\lambda_{K\gamma}$ ($\equiv c/\nu_{K\gamma}$),

$$\left[\frac{\partial f}{\partial \left(\frac{\lambda}{\lambda_{K\gamma}} \right)} \right]_{\lambda_{K\gamma}} = \frac{1}{2} \left(1 - \frac{\alpha_1/\sigma}{2} \right). \quad (9)$$

The values of p can be found empirically by means of the relation

$$p = \frac{E_A}{E_K} \cdot \frac{\lambda}{\lambda_K} - 1.$$

Values of $\log_{10} p$ obtained in this way are given in the following Table :—

| | | | | | | |
|---|-------|-------|--------|--------|--------|--------|
| $\lambda \times 10^8$ | | 0.87 | 0.71 | 0.56 | 0.49 | 0.35 |
| $\log_{10} p$ | | 0 | -0.042 | -0.126 | -0.195 | -0.320 |
| $\frac{\lambda_{K\gamma} - \lambda}{\lambda}$ | | 0.056 | 0.296 | 0.643 | 0.878 | 1.630 |

I can find no record of the wave-lengths of the K_γ line for bromine having been measured; but Friman* records a line L_{B_1} for this element for which $\lambda = 8.141 \times 10^{-8}$ cm. Using Kossel's relation we can assume as a sufficient approximation

$$\nu_{K\gamma} = \nu_K + \nu_{L_{B_1}} \quad (10)$$

and, putting $\lambda_{K\gamma} = 1.038 \times 10^{-8}$, this gives

$$\nu_{K\gamma} = 3.27 \times 10^{18} \text{ sec}^{-1} \text{ and } \lambda_{K\gamma} = 0.918 \times 10^{-8} \text{ cm.} \quad (11)$$

* 'Phil. Mag.', vol. 32, p. 497 (1916).

This value gives the data in the third row of the preceding Table.

On plotting the values of $\log p$ against $\frac{\lambda_{K\gamma}}{\lambda} - 1$, it appears that they can be represented, if not with absolute accuracy, at any rate to within the degree of accuracy of the measurements, by a single term of (6), viz., the term for which the index $\sigma_y = 1$. After determining the coefficient it appears that

$$p = e^{-0.460[(\lambda_{K\gamma}-\lambda)/\lambda]} = 10^{-0.200[(\lambda_{K\gamma}-\lambda)/\lambda]}. \quad (12)$$

Substituting in (9) this gives

$$-\left[\frac{\partial f}{\partial \left(\frac{\lambda}{\lambda_K} \right)} \right]_{\lambda_{K\gamma}} = 0.385. \quad (13)$$

The value of this differential coefficient measured from the curve on p. 336 of Barkla's paper is 0.376, which agrees satisfactorily with (13).

The complete expression for the fraction of the absorbed radiation which is transformed into fluorescent radiation of the K series is thus:—

$$\frac{E_K}{E_A} = \frac{\lambda}{(1+p)\lambda_K} = \frac{\lambda}{(1+e^{-0.46[(\lambda_{K\gamma}-\lambda)/\lambda]})\lambda_K}. \quad (14)$$

The values calculated from this formula are given in the fourth column of the following table:—

| λ . | p . | λ/λ_K . | $\frac{E_K}{E_A} = \frac{\lambda}{(1+p)\lambda_K}$ | $\frac{E_K}{E_A}$ observed. | Percentage error. | VII. |
|------------------------------|-------|-----------------------|--|-----------------------------|-------------------|------|
| $1.035 \times 10^{-8} \dots$ | | 1.00 | | | | |
| $0.87 \times 10^{-8} \dots$ | 0.973 | 0.84 | 0.426 | 0.42 | +1.4 | +2.4 |
| $0.71 \times 10^{-8} \dots$ | 0.871 | 0.686 | 0.368 | 0.36 | +2.2 | +5.6 |
| $0.56 \times 10^{-8} \dots$ | 0.743 | 0.542 | 0.312 | 0.31 | +0.65 | +6.5 |
| $0.49 \times 10^{-8} \dots$ | 0.667 | 0.473 | 0.285 | 0.29 | -1.7 | +6.9 |
| $0.35 \times 10^{-8} \dots$ | 0.472 | 0.338 | 0.230 | 0.23 | 0.0 | +8.7 |

For comparison the observed values of E_K/E_A are shown in the fifth column. The next column shows the difference of these numbers expressed as a percentage of the observed value. In every case the agreement is within the probable limits of the errors of measurement and is best for the shorter waves, where the measurements are admittedly most accurate. The last column gives the percentage error given by the corresponding numbers which Barkla calculates from his formula in column III of Table VIII on p. 345 of his paper. It will be seen that this formula gives a worse agreement in every single instance, and I suspect that the disagreement exceeds the probable errors of measurement in the case of the shorter waves. Moreover, all the deviations are in the same direction, and are greatest for the shorter waves, for which the experiments are most accurate.

It will be observed that the formula (14) for E_K/E_A contains only one arbitrary constant, the constants λ_K and $\lambda_{K\gamma}$ being predetermined by the X-ray spectrum of the atom. If, as the experiments seem to prove, the emission of fluorescent K-radiations is bound up with the simultaneous emission of electrons from positions near the surface of the atom, it is difficult to see how the complete expression for E_K/E_A can avoid containing at least one constant depending on the configuration of the electrons in the atom, in addition to the constants ν_K and $\nu_{K\gamma}$, which, as is shown by the success of Bohr's theory, merely involve energy relations.

Another view of the phenomena, which could be made to give expressions having some resemblance to those obtained, would be to suppose that radiation generated by the displacement of an electron to the central regions of an atom is liable to special absorption by the external electrons of the atom in which it is generated. One would naturally expect such absorption to be greatest for the softer rays in the neighbourhood of $\nu = \nu_{K\gamma}$, and to diminish to zero as ν approached infinity. However, I feel that this view contains an element of artificiality which it is undesirable to introduce into the interpretation of the phenomena, unless their more exact investigation makes it necessary.

As regards the precise form found for p , it does not seem wise to attempt to push the interpretation of this too far at present. The expression given certainly covers the experimental numbers to within the limits of experimental error, but it does not cover them exactly, and it is possible that a more precise experimental investigation of the formula would lead to a function which, whilst it would have to agree very closely with the expression found over the range of data now available, might have a different mathematical form, and consequently be capable of a different physical interpretation.

The main conclusions to be drawn from this paper may be summarised as follows :—

(1) The ratio E_K/E_A of the energy E_K emitted in the form of K secondary X-radiation to the energy E_A of the primary radiation (wave-length λ) absorbed is found, in the case of bromine, to be expressed to within the degree of accuracy of the observations by the formula

$$E_K/E_A = \frac{\lambda}{(1+p)\lambda_K},$$

where $p = e^{-0.46(\lambda_{K\gamma} - \lambda)/\lambda}$, λ_K is the average wave-length of the K radiations, and $\lambda_{K\gamma}$ is the wave-length of the shortest K radiation.

(2) The formula implies, or, at any rate, can be so interpreted as to

imply, the emission of one electron for every quantum ($h\nu$) of primary radiation absorbed. It likewise involves, for the emission of each quantum of K radiation, the absorption of one quantum of primary radiation when $\nu = \infty$, of two quanta of primary radiation when $\nu = \nu_{K\gamma}$, the limiting frequency (threshold frequency) for excitation, and of amounts of primary energy varying between one and two quanta for exciting radiations of intermediate frequency.

(3) Inasmuch as the formulae have been deduced, and have been given a plausible explanation, on the hypothesis that the primary radiation is absorbed in whole quanta, it does not appear that the facts under consideration can be held to support the contrary hypothesis.

[*Note added February 22, 1918.*—To these considerations may be added the general argument which is indicated, although perhaps insufficiently emphasised, in the preliminary part of this paper, and to which I have for some time felt that very great weight should be attached. It will be observed that, in the interpretation of the phenomena under discussion, both as given in this paper and as given by Prof. Barkla, and, in fact, in any reasonable interpretation of such phenomena, the quantity $h\nu$, where ν is the frequency of the exciting radiation, plays a conspicuous part. Now, the quantity ν has nothing whatever to do with the particular kind of matter with which the radiation reacts; it is a quantity whose value is determined by the radiation alone. It follows that the quantum relation is dominated by something in the structure or properties of radiation, although it may be that the limitations imposed by such structure or properties are inoperative except in regard to certain reactions with matter, such as absorption or emission, whereby the frequency of the radiation may be altered.]
